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(54) Diffractive optical element and optical system having the same

Beugungselement und damit ausgestattetes optisches System

Elément optique diffractif et système optique l'utilisant

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Description**FIELD OF THE INVENTION AND RELATED ART**

[0001] This invention relates to a diffractive optical element and an optical system having the same. More particularly, the invention is concerned with a diffractive optical element of good durability and small change in shape with time, thus providing diffractive light in particular direction with high diffraction efficiency. The present invention is particularly suitable for an optical system in a device manufacturing exposure apparatus, for example, having a light source of ArF excimer laser or KrF excimer laser, for example.

[0002] Chromatic aberration of an optical system can be reduced by using a physical phenomenon that, if a diffractive optical element having a light diffracting function is provided on a lens surface or in a portion of the optical system, then, with respect to light rays of a certain reference wavelength, the chromatic aberration is produced inversely ("SPIE Vol.1354, International Lens Design Conference (1990)", Japanese Laid-Open Patent Applications, Laid-Open Nos. 4-213421 and 6-324262, U.S. Patent No. 5,044,706, etc.).

[0003] Generally, in such diffractive optical element, a diffraction grating having periodic structure is formed rotationally symmetrically with respect to a certain axis such as an optical axis, and the period pitch of the diffraction grating is gradually changed. The ring zone structure having such periodic structure produces diffraction function which serves as a lens.

[0004] Such diffractive optical element provides good correction effect particularly to chromatic aberration which is produced at a refractive surface due to dispersion of glass. By changing the period of the periodic structure, an effect of aspherical surface lens can be provided. Thus, it is very effective for aberration reduction.

[0005] A specific structure of a diffractive optical element that produces such diffraction function is called "Kinoform". Examples are: one with portions for producing a phase difference 2π and being made continuous; one with binary shape (stepping shape) wherein continuous phase difference distribution is approximated by a stepping shape; and one wherein minute periodic structure is approximated by a triangular wave shape.

[0006] Such diffractive optical element can be manufactured through a semiconductor process (lithography, for example) or a cutting process.

[0007] Among these diffractive optical elements, a diffractive optical element of stepping shape (binary shape) is called a "binary optics (BO)", and a very fine structure can be manufactured through a semiconductor process such as lithography.

[0008] As an example, quartz may be used as a substrate for a binary optics; an i-line stepper may be used for an exposure process (printing a periodic pattern); a parallel flat plate type RIE apparatus may be used for a

dry etching process; then, through photolithography, a binary optics of ring-like pattern wherein each ring comprises eight steps (levels) may be produced. However, when a binary optics is manufactured by directly processing a quartz substrate, the quartz substrate may absorb a portion of intense light energy (e.g., laser light from a ArF or KrF excimer laser), causing compaction (contraction) thereof. This results in deformation of the shape of the binary optics.

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SUMMARY OF THE INVENTION

[0009] It is an object of the present invention to provide a diffractive optical element which does not cause compaction or large compaction, when it is irradiated with intense light energy.

[0010] It is another object of the present invention to provide an optical system having such diffractive optical element.

[0011] In accordance with an aspect of the present invention, there is provided a diffractive optical element, comprising: a substrate made of a fluoride compound; and a diffraction grating formed on the substrate by use of an oxide compound (oxide).

[0012] The diffraction grating may consist only of an oxide compound.

[0013] The diffraction grating may have a multilayered structure comprising the oxide compound and a fluoride compound, or a multilayered structure comprising the oxide compound and a metal oxide.

[0014] The diffraction grating may preferably comprise a binary optics.

[0015] The oxide compound may preferably consist of quartz or silica (SiO_2).

[0016] The oxide compound may consist of metal oxide such as alumina, cryolite, MgO , TiO_2 or HfO_2 .

[0017] The fluoride compound for the substrate may preferably comprise calcium fluoride (CaF_2 , fluorite).

[0018] The fluoride compound for the substrate may comprise AlF_3 , BaF_2 , LiF and MgF_2 .

[0019] A layer of oxide compound in the multilayered structure may serve mainly to provide a grating of stepped shape, and a layer of fluoride compound or metal oxide may serve as a stopper in a process for etching the oxide compound.

[0020] The fluoride compound in the multilayered structure, having served as an etching stopper, may comprise at least one of magnesium fluoride, lead fluoride, neodymium fluoride, lithium fluoride, lanthanum fluoride, calcium fluoride, barium fluoride, and aluminum fluoride.

[0021] The metal oxide in multilayered structure, having served as an etching stopper, may comprise at least one of aluminum oxide, magnesium oxide, hafnium oxide, neodymium oxide and cerium oxide.

[0022] In one preferred form of diffractive optical element of the present invention, an anti-reflection film is formed on the surface of the substrate on which the dif-

fraction grating is provided. The back surface of the substrate may also be provided with an anti-reflection film. [0023] These and other objects, features and advantages of the present invention will become more apparent upon a consideration of the following description of the preferred embodiments of the present invention taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024]

Figure 1 is a schematic view of a main portion of a diffractive optical element according to a first embodiment of the present invention.

Figures 2A and 2B are sectional views, respectively, of a portion of Figure 1.

Figure 3 is a schematic view for explaining a multi-layered film of a diffractive optical element according to the present invention.

Figure 4 is a schematic view for explaining a process for making a diffraction grating in a diffractive optical element according to the present invention. Figure 5 is a sectional view for explaining a diffractive optical element according to a second embodiment of the present invention.

Figure 6 is a perspective view of a binary optics according to a third embodiment of the present invention.

Figure 7 is a sectional view of the binary optics of the Figure 6 embodiment.

Figure 8 is an enlarged view of a portion of the sectional view of Figure 7, showing an example wherein one ring zone is defined by eight steps (levels).

Figure 9 is a schematic and sectional view for explaining a substrate, for the binary optics shown in Figures 6 - 8, prior to formation of a diffraction grating.

Figure 10 is a schematic view for explaining a process of manufacturing the binary optics shown in Figures 6 - 8.

Figure 11 is a schematic view of a diffractive optical element according to a fourth embodiment of the present invention, wherein an anti-reflection film is formed on a diffraction grating of binary optics such as shown in Figures 6 - 8.

Figure 12 is a schematic view of a projection exposure apparatus.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0025] Figure 1 is a schematic view of a main portion of a diffractive optical element according to a first embodiment of the present invention. Denoted at 1 in the drawing is a diffractive optical element.

[0026] The diffractive optical element 1 comprises a binary optics lens (a lens provided by a binary optics),

having a diffraction grating with lens function. However, the present invention is applicable also to diffractive optical element which comprises a Fresnel diffraction grating or a teeth-like diffraction grating, for example.

[0027] Typically, the sectional shape of the diffraction grating may be a stepped shape (binary shape) such as illustrated in the sectional view of Figure 2A of this embodiment, or a Kinoform shape such as illustrated in the sectional view of Figure 2B. However, the shape is not limited to them.

[0028] Figure 3 is a schematic and sectional view of a substrate to be used for manufacturing a diffractive optical element of the first embodiment, that is, in a state prior to making a diffraction grating thereon. The substrate 2 of the diffractive optical element 1 of this embodiment consists of a fluoride compound such as fluorite, for example. Diffraction grating 1a to be provided on the substrate 2 is made of quartz or silica (SiO_2) 4 and a fluoride compound 5 such as fluorite (calcium fluoride), for example. These materials are accumulated into a multilayered film 3 and, by etching the film 3, a diffraction grating such as shown in Figure 2A is provided.

[0029] Here, the silica layer 4 serves mainly to provide steps through dry etching, while the fluoride compound layer 5 serves, in the dry etching process for the silica layer 4, as a stopper for controlling the amount of etching.

[0030] In this embodiment, in place of conventionally used quartz, use is made of fluorite (fluoride compound) 30 for the substrate of a diffractive optical element. As compared with quartz, fluorite has an advantage of small compaction (contraction). Also, it provides correction of chromatic aberration. Thus, fluorite is a material suitable for a binary optics lens in an imaging optical system. 35 However, as compared with quartz, it has a lower stiffness. Therefore, as compared with quartz, dry etching is not easy.

[0031] In this embodiment, in consideration of the above, a thin film of quartz or silica (oxide compound) 40 which can be dry etched easily is provided on the surface of a fluorite (fluoride compound) substrate. Then, by using a photolithography process and a dry etching process, a diffraction grating is defined on such silica thin film.

[0032] Silica thin film may be formed on the basis of sputtering film forming method, EB film forming method, or CVD film forming method, for example. In this embodiment, the sputtering film forming method is used to produce a binary optics, because of its ease in handling.

[0033] In this embodiment, in order to meet difficulty in etching control in depth direction which otherwise may cause degraded surface property of the etched surface, seven silica layers of a thickness corresponding to the binary steps may be formed beforehand, and a thin film

55 layer that functions as an etching stopper may be provided at the boundary between the steps (i.e., between silica layers).

[0034] As for the material of such thin film, it may be

a material having resistivity to an etching gas, for etching the silica, and having a property that, when the etching gas is replaced by another, then the silica shows resistivity. Since generally metal fluoride has a resistivity to halogen series etching gas, it may suitably used as a material for silica film RIE etching stopper. Thus, in this embodiment, fluoride compound, particularly, fluoride compound having good transmissivity to deep ultraviolet rays such as magnesium fluoride, lead fluoride, neodymium fluoride, lithium fluoride, lanthanum fluoride, calcium fluoride, or barium fluoride, for example, may be used as an etching stopper, by which a corresponding fluoride metal film of about 100 angstroms may be formed on the surface of each silica thin film layer. This enables a binary optics lens with fluorite base, having good shape precision and good surface property, under tolerant etching condition.

[0035] A specific structure of the diffractive optical element 1 in the first embodiment will be described below.

[0036] The diffractive optical element (binary optics lens) 1 of the first embodiment had a circular outside shape with a diameter 20mm Ø. This optical element is adapted for use with light of a wavelength 248 nm from a KrF excimer laser, and thus its design wavelength is 248 nm. The total number of rings of the diffraction grating of this optical element was about 1800. Each ring comprised eight-step shape element (unit) such as shown in Figure 2A.

[0037] In the binary optics lens of Figure 2A, in the design value the steps constituting the outermost ring has a width (of each step) Wa of 0.35 micron and a height Ha of 0.062 micron. The width Wa of the ring (i.e., the whole steps) and the height Ha thereof were Wa = 2.8 micron (= 0.35 micron x 8) and Ha = 0.434 micron (= 0.062 micron x 7), respectively.

[0038] As for the substrate 2, a crystal substrate of fluorite of a diameter 4 inches (100mm) and a thickness 4 mm was used. By using a sputtering apparatus for multi-sputtering and in accordance with continuous film forming method, silica (SiO_2) 4 of about 520 angstroms and barium fluoride 5 (i.e., metal fluoride) of about 100 angstroms were formed on the substrate. The total film thickness was about 620 angstroms. A pair of one silica layer and one barium fluoride layer provides one step of the eight-step binary optics. The operation was repeated seven times, whereby seven accumulated layers (each comprising a pair) having a thickness of about 0.434 micron, were produced.

[0039] The diffraction grating 1a having eight steps per unit can be produced by using an i-line stepper ($\lambda = 365$ nm) on the above-described fluorite substrate with seven-layer multilayered film. More specifically, as shown at the upper half of Figure 4, patterns of chromium masks 11, 12 and 13 are printed sequentially on a photoresist on the binary optics substrate 2, each printing being followed by development of photoresist and dry etching (RIE) process using the developed resist pattern as a mask, whereby the multilayered film 3 on

the fluorite substrate 2 can be etched and patterned. Since the fluorite 5 of the substrate 2 has resistivity to a halogen series etching gas, the bottom step does not need an etching stopper film. The lower half of Figure 4 shows that, with the result of repeating the above-described process three times by using the three masks 11, 12 and 13 sequentially, a binary optics lens having a diffraction grating structure with eight-step unit for each ring can be produced on the substrate 2.

10 [0040] A modified form of the first embodiment will be described below.

[0041] The diffractive optical element 1 of this modified form had a circular outside shape with a diameter 20mm, like the first embodiment of Figure 1. In place of the barium fluoride of the first embodiment, this modified form used calcium fluoride.

[0042] As for the substrate 2, a crystal substrate of fluorite of a diameter 4 inches (100mm) and a thickness 4 mm was used. By using a sputtering apparatus for 20 multi-sputtering and in accordance with continuous film forming method, silica (SiO_2) 4 of about 520 angstroms and calcium fluoride 5 (i.e., metal fluoride) of about 100 angstroms were formed on the substrate. The total film thickness was about 620 angstroms. The operation was 25 repeated seven times, whereby seven accumulated layers having a thickness of about 0.434 micron, were produced.

[0043] The binary optics lens 1 can be produced by using an i-line stepper ($\lambda = 365$ nm) on the above-described fluorite substrate with seven-layer multilayered film. More specifically, as shown at the upper half of Figure 4, patterns of chromium masks 11, 12 and 13 are printed sequentially on a photoresist on the binary optics substrate 2, each printing being followed by development of photoresist and dry etching (RIE) process using the developed resist pattern as a mask, whereby the multilayered film 3 on the fluorite substrate 2 can be etched and patterned. As an etching gas, a gas mainly containing CCl_2F_2 , CF_4 and BCl_3 , was used. The above-described process was repeated three times by using the three masks 11, 12 and 13 sequentially, whereby a binary optics lens was produced.

[0044] Another modified form of the first embodiment will be described below.

[0045] The diffractive optical element 1 of this modified form had a circular outside shape with a diameter 20mm, like the first embodiment. In place of barium fluoride in the first embodiment, this modified form used aluminum fluoride (AlF_3), and seven-layer multilayered 50 film of silica (SiO_2) and aluminum fluoride was formed on a fluorite substrate 2. Like the first embodiment, through a photolithographic process, a binary optics lens was produced.

[0046] A further modified form of the first embodiment will be described below.

[0047] A diffractive optical element 1 of this modified form comprises, like the first embodiment of Figure 1, a fluorite substrate 2 on which a seven-layer multilayered

film of quartz (SiO_2) and fluoride compound (metal fluoride of one of magnesium fluoride, lead fluoride, neodymium fluoride, lithium fluoride, lanthanum fluoride, cryolite, etc.) is formed. Through a photolithographic process similar to the first embodiment, a binary optics lens was produced.

[0048] Next, a second embodiment of the present invention will be described. A diffractive optical element according to the second embodiment is like that shown in Figure 1 of the first embodiment. Also in the second embodiment, the diffractive optical element comprises a binary optics lens having a diffraction grating with lens function. However, the present invention is applicable also to a diffractive optical element having a Fresnel diffraction grating or a teeth-like diffraction grating, for example.

[0049] Typically, the sectional shape of the diffraction grating may be a stepped shape (binary shape) such as illustrated in the sectional view of Figure 2A, or a Kinoform shape such as illustrated in the sectional view of Figure 2B. However, the shape is not limited to them.

[0050] Figure 5 is a schematic and sectional view of a substrate to be used for manufacturing a diffractive optical element of the second embodiment. The substrate 2 of the diffractive optical element 1 of this embodiment consists of a fluoride compound such as fluorite, for example. Diffraction grating 1a to be provided on the substrate 2 is made of quartz or silica (SiO_2) 4 and a metal oxide 5 such as aluminum oxide (Al_2O_3), for example. These materials are accumulated into a multi-layered film 3 and, by etching the film 3, a diffraction grating such as shown in Figure 2A is provided.

[0051] Here, the silica layer 4 serves mainly to provide steps through dry etching, while the metal oxide layer 5 serves, in the dry etching process for the silica layer 4, as a stopper for controlling the amount of etching.

[0052] In this embodiment, in place of conventionally used quartz, use is made of fluorite (fluoride compound) for the substrate of a diffractive optical element. As compared with quartz, fluorite has an advantage of small compaction (contraction). Also, it provides correction of chromatic aberration. Thus, fluorite is a material suitable for a binary optics lens in an imaging optical system. However, as compared with quartz, it has a lower stiffness. Therefore, as compared with quartz, dry etching is not easy.

[0053] In this embodiment, in consideration of the above, a thin film of quartz or silica (silicon oxide) which can be dry etched easily is provided on the surface of a fluorite (fluoride compound) substrate. Then, by using a photolithography process and a dry etching process, a diffraction grating is defined on such silica thin film.

[0054] Silica thin film may be formed on the basis of sputtering film forming method, EB film forming method, or CVD film forming method, for example. In this embodiment, the sputtering film forming method is used to produce a binary optics, because of its easiness in handling.

[0055] In this embodiment, in order to meet difficulty in etching control in depth direction which otherwise may cause degraded surface property of the etched surface, silica layers of a thickness corresponding to the binary steps may be formed beforehand, and a thin film layer that functions as an etching stopper may be provided at the boundary between the steps (i.e., between silica layers).

[0056] As for the material of such thin film, it may be a material having resistivity to an etching gas, for etching the silica, and having a property that, when the etching gas is replaced by another, then the silica shows resistivity. Thus, in this second embodiment, metal oxide, particularly, metal oxide having good transmissivity to deep ultraviolet rays such as aluminum oxide may be used, by which a corresponding aluminum oxide film of about 100 angstroms may be formed on the surface of each thin film layer. This enables a binary optics lens with fluorite base, having good shape precision and good surface property, under tolerant etching condition.

[0057] A specific structure of the diffractive optical element 1 in the second embodiment will be described below.

[0058] The diffractive optical element (binary optics lens) 1 of the second embodiment had a circular outside shape with a diameter 20mm \varnothing . This optical element is adapted for use with light of a wavelength 248 nm from a KrF excimer laser, and thus its design wavelength is 248 nm. The total number of rings of the diffraction grating of this optical element was about 1800. Each ring comprised eight-step shape element (unit) such as shown in Figure 2A.

[0059] In the binary optics lens of Figure 2A, showing binary optics lens element unit 1a, in the design value the steps constituting the outermost ring has a width (of each step) W_{al} of 0.35 micron and a height H_{al} of 0.062 micron. The width W_{a} of the ring (i.e., the whole steps) and the height H_{a} thereof were $W_{\text{a}} = 2.8$ micron (= 0.35 micron \times 8) and $H_{\text{a}} = 0.434$ micron (= 0.062 micron \times 7), respectively.

[0060] As for the substrate 2, a crystal substrate of fluorite of a diameter 4 inches (100mm) and a thickness 4 mm was used. By using a sputtering apparatus for multi-sputtering and in accordance with continuous film forming method, silica (SiO_2) 4 of about 520 angstroms and aluminum oxide (Al_2O_3) (i.e., metal oxide) of about 100 angstroms were formed on the substrate. The total film thickness was about 620 angstroms. A pair of one silica layer and one aluminum oxide layer provides one step of the eight-step binary optics element. The operation was repeated seven times, whereby seven accumulated layers having a thickness of about 0.434 micron, were produced.

[0061] The diffraction grating 1a having eight steps per unit can be produced by using an i-line stepper ($\lambda = 365$ nm) on the above-described fluorite substrate with seven-layer multilayered film, similarly to the first embodiment. More specifically, as shown in Figure 4, pat-

terns of chromium masks 11, 12 and 13 are printed sequentially on a photoresist on the binary optics substrate 2, each printing being followed by development of photoresist and dry etching (RIE) process using the developed resist pattern as a mask, whereby the multilayered film 3 on the fluorite substrate 2 can be etched and patterned. Since the fluorite 5 of the substrate 2 has resistivity to a halogen series etching gas, the bottom step does not need an etching stopper film.

[0062] A modified form of the second embodiment will be described below.

[0063] The diffractive optical element 1 of this modified form had a circular outside shape with a diameter 20mm. In place of the aluminum oxide (Al_2O_3) of the second embodiment, this modified form used MgO .

[0064] As for the substrate 2, a crystal substrate of fluorite of a diameter 4 inches (100mm) and a thickness 4 mm was used. By using a sputtering apparatus for multi-sputtering and in accordance with continuous film forming method, silica (SiO_2) 4 of about 520 angstroms and magnesium oxide 5 (i.e., metal oxide) of about 100 angstroms were formed on the substrate. The total film thickness was about 620 angstroms. The operation was repeated seven times, whereby seven accumulated layers having a thickness of about 0.434 micron, were produced.

[0065] The binary optics lens 1 can be produced by using an i-line stepper ($\lambda = 365 \text{ nm}$), like the second embodiment. More specifically, as shown in Figure 4, patterns of chromium masks 11, 12 and 13 are printed sequentially on a photoresist on the binary optics substrate 2, each printing being followed by development of photoresist and dry etching (RIE) process using the developed resist pattern as a mask, whereby the multilayered film 3 on the fluorite substrate 2 can be etched and patterned. As an etching gas, a gas mainly containing CCl_2F_2 and CF_4 was used. The above-described process was repeated three times by using the three masks 11, 12 and 13 sequentially, whereby a binary optics lens was produced.

[0066] Another modified form of the second embodiment will be described below.

[0067] The diffractive optical element 1 of this modified form had a circular outside shape with a diameter 20mm. In place of aluminum oxide in the second embodiment, this modified form used neodymium oxide, and seven-layer multilayered film of silicon oxide (SiO_2) and neodymium oxide was formed on a fluorite substrate 2. Like the second embodiment, through a photolithographic process, a binary optics lens was produced.

[0068] A further modified form of the second embodiment will be described below.

[0069] A diffractive optical element 1 of this modified form comprises, like the second embodiment, a fluorite substrate 2 on which a seven-layer multilayered film of quartz (SiO_2) and metal oxide of one of hafnium oxide and cerium oxide, for example, is formed. Through a

photolithographic process similar to the second embodiment, a binary optics lens was produced.

[0070] It is to be noted that, even if the third dry etching process is made slightly excessively, the resistivity as an etching stopper of the barium fluoride substrate 2 is effective to assure good finishing with good precision.

[0071] In one preferred form of the present invention, as for the substrate 2, fluorite may be replaced by a crystal of magnesium fluoride (MgF_2) and a thin film 3 of silica may be provided on the magnesium fluoride substrate 2. Through a photolithographic process and a dry etching process, like the second embodiment, a binary optics lens of 20 mm diameter can be produced.

[0072] Figure 11 is a sectional view of a diffractive optical element according to another preferred form of the present invention. In this example, like the preceding example, a thin film 3 of silica is formed on a fluorite substrate 2, and, through a similar photolithographic process and a similar dry etching process, a binary optics

lens of eight-step structure is produced. After this, anti-reflection coatings 8 are formed on opposite surfaces of the binary optics lens. The anti-reflection film 8 was provided by a layer of lithium fluoride (LiF) deposited by 62 nm through RF sputtering method, for example. Diffraction efficiency of the resultant binary optics lens was measured by using KrF laser, and the result is that, as compared with an element without anti-reflection film on opposite surfaces, the diffraction efficiency was improved by about 12%.

[0073] In another preferred form of the present invention which may correspond to a modified form of the preceding example, magnesium fluoride and alumina (Al_2O_3) were deposited by RF sputtering method, each with a thickness 62 nm, whereby an anti-reflection coating 8 was formed. With this anti-reflection film 8, the diffraction efficiency was improved by about 16% as compared with the element without anti-reflection film on opposite surfaces thereof.

[0074] It is to be noted that use of such anti-reflection coating is effective in any of the first and second embodiments and in any of modified forms described above. Such anti-reflection coating may be provided on only one surface of the substrate, if desired.

[0075] Figure 12 is a schematic view of an optical arrangement of a projection exposure apparatus. There are, in an order from the above, a light source 11 such as a lamp or laser, an illumination optical system 12 for providing uniform illumination by use of light from the light source 11, a reticle R to be illuminated with the illumination optical system 12, a projection optical system 13 for projecting a pattern formed on the reticle R onto a wafer W, and the wafer W on which the pattern is to be projected by the projection optical system 13.

[0076] A third embodiment of the present invention will be described with reference to Figures 6 - 11.

[0077] Figure 6 is a perspective view of a binary optics lens having ring-like diffraction elements (steps). Figure 7 is a sectional view of the binary optics lens, and Figure

8 is an enlarged view of a portion of Figure 7. As designed, the binary optics lens is to be used with KrF laser light of used wavelength 248 nm, and it has rings as diffraction element unit of a number of about 1800. Each ring has eight steps (levels) such as shown in Figure 8, and the whole structure provides a binary optics lens 1 of circular shape, with a diameter 20 mm. In the design value, the steps constituting the outermost ring each has a width W_{al} of 0.35 micron and a height H_{al} of 0.062 micron. The width of ring as the unit of diffraction element is 2.8 microns, and the height is 0.434 micron.

[0078] Figure 9 is a sectional view of a substrate, prior to production of binary optics lens of the third embodiment. In this embodiment, a crystal plate of fluorite (CaF_2) of a diameter 100 mm and a thickness 4mm is used. By using a sputtering apparatus, a thin film 7 of silica (SiO_2) which can be dry etched easily is formed on the surface of the fluorite substrate 2, to a thickness of about 0.434 micron, corresponding to the level difference of the binary optics. In place of sputtering film forming method, EB film forming method or CVD film forming method may be used.

[0079] Figure 10 is a sectional view of chromium masks to be used for forming eight fine steps on the silica thin film 3 of the substrate of the binary optics lens, as well as of the binary optics lens to be produced thereby. An i-line stepper (exposure wavelength $\lambda = 365 \text{ nm}$) which is a photolithographic reduction exposure printing apparatus is used to print a pattern of the chromium mask 4 on a photoresist of the substrate 2 in reduced scale, and the exposed substrate is developed, whereby a resist pattern is defined. Dry etching process is then performed while the resist pattern is used as a mask, whereby the thin film 3 of the substrate 2 is etched and patterned, such that steps are defined thereon. Subsequently, while using the chromium masks 5 and 6, the above-described procedure is repeated, whereby steps (7) are produced in the thin film 7 and a binary optics lens 1 is produced.

[0080] Fluoride compound as represented by fluorite generally has resistivity to a dry etching gas such as halogen gas, for example, and thus it functions as an etching stopper. Therefore, a high precision binary optics lens for which substantially vertical steps are required, can be produced.

[0081] In a modified form of the third embodiment, in place of the fluorite substrate 2, a crystal plate 2 of barium fluoride of a diameter 100 mm and a thickness 4 mm, may be used. By using an RF sputtering apparatus, a silica thin film 7 may be formed on the substrate 2 with a thickness of about 0.43 micron, whereby a binary optics lens 1 of circular shape having a diameter 20 mm, can be produced.

[0082] Also in that occasion, an i-line stepper is used to print a pattern of a chromium mask on a photoresist of the substrate 2 of barium fluoride with silica thin film, in reduced scale, and the exposed substrate is developed, whereby a resist pattern is defined. Dry etching

process is then performed while the resist pattern is used as a mask, whereby the thin film 3 of the barium fluoride substrate 2 is etched and patterned and a binary optics lens is produced. As an etching gas, a gas mainly consisting of CF_4/H_2 and CH_2F_2 is used, and the above-described process is repeated three times by using three masks 4 and 5, whereby a binary optics lens 1 is provided.

[0083] As regards the shape of the substrate 2 in the binary optics lenses having been described above, the substrate may have flat surfaces on opposite sides, a flat surface on one side only, or curved surfaces on opposite sides.

[0084] Referring back to Figure 12, a binary optics lens to be used in this exposure apparatus may be any one of the binary optics lenses having been described above. Through divided exposures by use of a stepper, a size of 200 mm diameter can be produced. Such a binary optics lens may be incorporated into the illumination optical system 12 or the projection optical system 13. With reduction printing of a silicone substrate through a KrF laser stepper of step-and-scan type or step-and-repeat type, and in accordance with sequential semiconductor manufacturing processes, high performance semiconductor devices can be produced.

[0085] Thus, use of such exposure apparatus enables production of good precision devices such as semiconductor devices (e.g., IC or LSI), liquid crystal devices, image pickup devices (e.g., CCD), magnetic devices (e.g., magnetic head), or optical elements (e.g., BOE).

Claims

35. 1. A diffractive optical element (1), comprising:
a substrate (2) made of a fluoride compound;
and
a diffraction grating (1a) formed on the substrate and comprising an oxide compound.
40. 2. A diffractive optical element according to Claim 1,
wherein the diffraction grating has a multilayered structure (4, 5) comprising the oxide compound and a second fluoride compound.
45. 3. A diffractive optical element according to Claim 2,
wherein the second fluoride compound is adapted to serve as a stopper in a process for etching the oxide compound.
50. 4. A diffractive optical element according to Claim 3,
wherein the second fluoride compound comprises at least one of magnesium fluoride, lead fluoride, neodymium fluoride, lithium fluoride, lanthanum fluoride, calcium fluoride, barium fluoride, and aluminum fluoride.

5. A diffractive optical element according to Claim 1, wherein the diffraction grating has a multilayered structure comprising the oxide compound and a metal oxide.

6. A diffractive optical element according to Claim 5, wherein the metal oxide is adapted to serve as a stopper in a process for etching the oxide compound.

7. A diffractive optical element according to Claim 6, wherein the metal oxide comprises at least one of aluminum oxide, magnesium oxide, hafnium oxide, neodymium oxide and cerium oxide.

8. A diffractive optical element according to Claim 1, wherein the oxide compound consists of one of silica, alumina, cryolite, MgO, TiO₂ and HfO₂.

9. A diffractive optical element according to Claim 1, wherein the substrate consists of one of CaF₂, AlF₃, BaF₂, LiF and MgF₂.

10. A diffractive optical element according to Claim 9, wherein the oxide compound consists of one of silica, alumina, cryolite, MgO, TiO₂ and HfO₂.

11. A diffractive optical element according to Claim 10, wherein the diffraction grating has a multilayered structure comprising the oxide compound and a second fluoride compound.

12. A diffractive optical element according to Claim 11, wherein the second fluoride compound is adapted to serve as a stopper in a process for etching the oxide compound.

13. A diffractive optical element according to Claim 12, wherein the second fluoride compound comprises at least one of magnesium fluoride, lead fluoride, neodymium fluoride, lithium fluoride, lanthanum fluoride, calcium fluoride, barium fluoride, and aluminum fluoride.

14. A diffractive optical element according to Claim 10, wherein the diffraction grating has a multilayered structure comprising the oxide compound and a metal oxide.

15. A diffractive optical element according to Claim 14, wherein the metal oxide is adapted to serve as a stopper in a process for etching the oxide compound.

16. A diffractive optical element according to Claim 15, wherein the metal oxide comprises at least one of aluminum oxide, magnesium oxide, hafnium oxide, neodymium oxide and cerium oxide.

17. A diffractive optical element according to Claim 10, wherein the substrate consists of CaF₂ and the oxide compound consists of silica.

5 18. A diffractive optical element according to Claim 17, wherein the substrate has an anti-reflection film formed on at least one surface thereof.

10 19. A diffractive optical element according to Claim 17, wherein the substrate has an anti-reflection film formed on opposite surfaces thereof.

15 20. A diffractive optical element according to Claim 1, wherein said diffractive optical element comprises a binary optics.

20 21. A diffractive optical element according to Claim 1, wherein at least one surface of the substrate is flat.

25 22. A diffractive optical element according to Claim 1, wherein the substrate has a curved surface.

23. An optical system having a diffractive optical element as recited in any one of Claims 1 - 22.

24. An exposure apparatus including an optical system as recited in Claim 23.

30 25. A device manufacturing method for transferring a device pattern onto a wafer by use of an exposure apparatus as recited in claim 24.

35 26. A method of producing a diffractive optical element comprising the steps of:

35 providing a substrate of a fluoride compound; providing a layer including an oxide compound on the substrate; and forming a diffractive optical pattern in the oxide compound layer by an etching process.

40 27. A method according to claim 26, wherein the layer including the oxide compound is a multilayered structure of oxide compound layers alternated with layers of a second fluoride compound or layers of a metal oxide, and the second fluoride compound or metal oxide layers act as etching stopper layers in the etching process.

45 50 28. A method according to claim 26 or claim 27, further comprising the step of forming an anti-reflection layer on one or both surfaces of the optical element.

55 **Patentansprüche**

1. Optisches Beugungselement (1) mit:

einem Substrat (2), das aus einer Fluoridverbindung hergestellt ist, und einem Beugungsgitter (1a), das an dem Substrat ausgebildet ist und eine Oxidverbindung aufweist.

2. Optisches Beugungselement gemäß Anspruch 1, wobei das Beugungsgitter eine Mehrlagenstruktur (4, 5) hat, die die Oxidverbindung und eine zweite Fluoridverbindung aufweist.

3. Optisches Beugungselement gemäß Anspruch 2, wobei die zweite Fluoridverbindung daran angepasst ist, dass sie als ein Stopper bei einem Prozess zum Ätzen der Oxidverbindung dient.

4. Optisches Beugungselement gemäß Anspruch 3, wobei die zweite Fluoridverbindung zumindest entweder Magnesiumfluorid, Bleifluorid, Neodymfluorid, Lithiumfluorid, Lanthanfluorid, Calciumfluorid, Bariumfluorid oder Aluminiumfluorid aufweist.

5. Optisches Beugungselement gemäß Anspruch 1, wobei das Beugungsgitter eine Mehrlagenstruktur hat, die die Oxidverbindung und eine Metallverbindung aufweist.

6. Optisches Beugungselement gemäß Anspruch 5, wobei das Metalloxid daran angepasst ist, das es als ein Stopper bei einem Prozess zum Ätzen der Oxidverbindung dient.

7. Optisches Beugungselement gemäß Anspruch 6, wobei das Metalloxid zumindest entweder Aluminiumoxid, Magnesiumoxid, Hafniumoxid, Neodynamoxid oder Cerioxid aufweist.

8. Optisches Beugungselement gemäß Anspruch 1, wobei die Oxidverbindung aus entweder Siliziumoxid, Tonerde (Alumina), Cryolit, MgO, TiO₂ oder HfO₂ besteht.

9. Optisches Beugungselement gemäß Anspruch 1, wobei das Substrat aus entweder CaF₂, AlF₃, BaF₂, LiF oder MgF₂ besteht.

10. Optisches Beugungselement gemäß Anspruch 9, wobei die Oxidverbindung aus entweder Siliziumoxid, Tonerde (Alumina), Cryolit, MgO, TiO₂ oder

HfO₂ besteht.

11. Optisches Beugungselement gemäß Anspruch 10, wobei das Beugungsgitter eine Mehrlagenstruktur hat, die aus der Oxidverbindung und einer zweiten Fluoridverbindung besteht.

12. Optisches Beugungselement gemäß Anspruch 11, wobei die zweite Fluoridverbindung daran angepasst ist, dass sie als ein Stopper bei einem Prozess zum Ätzen der Oxidverbindung dient.

13. Optisches Beugungselement gemäß Anspruch 12, wobei die zweite Fluoridverbindung zumindest entweder Magnesiumfluorid, Bleifluorid, Neodymfluorid, Lithiumfluorid, Lanthanfluorid, Calciumfluorid, Bariumfluorid oder Aluminiumfluorid aufweist.

14. Optisches Beugungselement gemäß Anspruch 10, wobei das Beugungsgitter eine Mehrlagenstruktur hat, die die Oxidverbindung und ein Metalloxid aufweist.

15. Optisches Beugungselement gemäß Anspruch 14, wobei das Metalloxid daran angepasst ist, das es als ein Stopper bei einem Prozess zum Ätzen der Oxidverbindung dient.

16. Optisches Beugungselement gemäß Anspruch 15, wobei das Metalloxid zumindest entweder Aluminiumoxid, Magnesiumoxid, Hafniumoxid, Neodynamoxid oder Cerioxid aufweist.

17. Optisches Beugungselement gemäß Anspruch 10, wobei das Substrat aus CaF₂ besteht und die Oxidverbindung aus Siliziumoxid besteht.

18. Optisches Beugungselement gemäß Anspruch 17, wobei das Substrat einen Antireflektionsfilm hat, der an zumindest einer Oberfläche von ihm ausgebildet ist.

19. Optisches Beugungselement gemäß Anspruch 17, wobei das Substrat einen Antireflektionsfilm hat, der an einer entgegengesetzten Oberfläche von ihm ausgebildet ist.

20. Optisches Beugungselement gemäß Anspruch 1, wobei

das optische Beugungselement eine Binärop-
tik aufweist.

21. Optisches Beugungselement gemäß Anspruch 1, wobei zumindest eine Oberfläche des Substrats flach ist. 5

22. Optisches Beugungselement gemäß Anspruch 1, wobei
das Substrat eine gekrümmte Oberfläche hat. 10

23. Optisches System mit einem optischen Beugungs-
element gemäß einem der Ansprüche 1 bis 22.

24. Belichtungsgerät mit einem optischen System ge-
mäß Anspruch 23. 15

25. Vorrichtungsherstellverfahren zum Übertragen ei-
nes Vorrichtungsmusters auf einen Wafer unter
Verwendung eines Belichtungsgeräts gemäß An-
spruch 24. 20

26. Verfahren zum Herstellen eines optischen Beu-
gungselements mit den folgenden Schritten:

Vorsehen eines Substrats aus einer Fluoridver-
bindung;
Vorsehen einer Lage, die eine Oxidverbindung
an dem Substrat umfasst;
Ausbilden eines optischen Beugungsmusters
in der Oxidverbindungsfrage durch einen Ätz-
prozess. 25

27. Verfahren gemäß Anspruch 26, wobei
die Lage, die die Oxidverbindung hat, eine
Mehrlagenstruktur aus Oxidverbindungsagen ist,
die mit Lagen einer zweiten Fluoridverbindung oder
Lagen eines Metalloxids sich abwechseln, und wo-
bei die Lagen der zweiten Fluoridverbindung oder
des Metalloxids als Ätzstopperlagen bei dem Ätz-
prozess wirken. 35

28. Verfahren gemäß Anspruch 26 oder Anspruch 27,
das des weiteren den folgenden Schritt aufweist:

Ausbilden einer Antireflexionslage an einer
oder beiden Oberflächen des optischen Ele-
ments. 40

2. Elément optique de diffraction selon la revendica-
tion 1, dans lequel le réseau de diffraction présente
une structure multicouche (4, 5), comportant le
composé d'oxyde et un second composé de fluorure.

3. Elément optique de diffraction selon la revendica-
tion 2, dans lequel le second composé de fluorure
est adapté pour servir de moyen d'arrêt dans un
procédé d'attaque chimique du composé d'oxyde.

4. Elément optique de diffraction selon la revendica-
tion 3, dans lequel le second composé de fluorure
comporte au moins un des éléments suivants : le
fluorure de magnésium, le fluorure de plomb, le
fluorure de néodyme, le fluorure de lithium, le fluo-
rure de lanthane, le fluorure de calcium, le fluorure
de baryum et le fluorure d'aluminium.

5. Elément optique de diffraction selon la revendica-
tion 1, dans lequel le réseau de diffraction présente
une structure multicouche comportant le composé
d'oxyde et un oxyde métallique.

6. Elément optique de diffraction selon la revendica-
tion 5, dans lequel l'oxyde métallique est adapté
pour servir de moyen d'arrêt dans un procédé d'at-
taque chimique du composé d'oxyde.

7. Elément optique de diffraction selon la revendica-
tion 6, dans lequel l'oxyde métallique comporte au
moins un des éléments suivants : l'oxyde d'alumi-
nium, l'oxyde de magnésium, l'oxyde d'hafnium,
l'oxyde de néodyme et l'oxyde de cérium.

8. Elément optique de diffraction selon la revendica-
tion 1, dans lequel le composé d'oxyde est constitué
d'un des éléments suivants : la silice, l'alumine, la
cryolite, MgO, TiO₂ et HfO₂.

9. Elément optique de diffraction selon la revendica-
tion 1, dans lequel le substrat est constitué d'un des
éléments suivants : CaF₂, AlF₃, BaF₂, LiF et MgF₂.

10. Elément optique de diffraction selon la revendica-
tion 1, dans lequel le composé d'oxyde est constitué
d'un des éléments suivants : la silice, l'alumine, la
cryolite, MgO, TiO₂ et HfO₂.

11. Elément optique de diffraction selon la revendica-
tion 10, dans lequel le réseau de diffraction pré-
sente une structure multicouche comportant le compo-
sé d'oxyde et un second composé de fluorure.

12. Elément optique de diffraction selon la revendica-
tion 11, dans lequel le second composé de fluorure
est adapté pour servir de moyen d'arrêt dans un
procédé d'attaque chimique du composé d'oxyde.

Revendications

1. Elément optique de diffraction (1), comportant :

un substrat (2) réalisé à partir d'un composé de
fluorure ; et
un réseau de diffraction (la) formé sur le subs-
trat et comportant un composé d'oxyde.

13. Elément optique de diffraction selon la revendication 12, dans lequel le second composé de fluorure comporte au moins un des éléments suivants : le fluorure de magnésium, le fluorure de plomb, le fluorure de néodyme, le fluorure de lithium, le fluorure de lanthane, le fluorure de calcium, le fluorure de baryum et le fluorure d'aluminium.	5
14. Elément optique de diffraction selon la revendication 10, dans lequel le réseau de diffraction présente une structure multicouche comportant le composé d'oxyde et un oxyde métallique.	10
15. Elément optique de diffraction selon la revendication 14, dans lequel l'oxyde métallique est adapté pour servir de moyen d'arrêt dans un procédé d'attaque chimique du composé d'oxyde.	15
16. Elément optique de diffraction selon la revendication 15, dans lequel l'oxyde de métal comporte au moins un des éléments suivants : l'oxyde d'aluminium, l'oxyde de magnésium, l'oxyde d'hafnium, l'oxyde de néodyme et l'oxyde de cérium.	20
17. Elément optique de diffraction selon la revendication 10, dans lequel le substrat est constitué de CaF ₂ et le composé d'oxyde est constitué de silice.	25
18. Elément optique de diffraction selon la revendication 17, dans lequel un film antiréfléchissant est formé sur au moins une surface du substrat.	30
19. Elément optique de diffraction selon la revendication 17, dans lequel un film antiréfléchissant est formé sur des surfaces opposées du substrat.	35
20. Elément optique de diffraction selon la revendication 1, dans lequel ledit élément optique de diffraction comporte une optique binaire.	40
21. Elément optique de diffraction selon la revendication 1, dans lequel au moins une surface du substrat est plate.	
22. Elément optique de diffraction selon la revendication 1, dans lequel le substrat a une surface courbe.	45
23. Système optique ayant un élément optique de diffraction selon l'une quelconque des revendications 1 à 22.	50
24. Appareil d'exposition comprenant un système optique selon la revendication 23.	
25. Procédé de fabrication de dispositif pour transférer un motif de dispositif sur une plaquette à l'aide d'un appareil d'exposition selon la revendication 24.	55
26. Procédé de production d'un élément optique de diffraction comportant les étapes consistant :	
à produire un substrat constitué d'un composé de fluorure ;	
à produire une couche comprenant un composé d'oxyde sur le substrat ; et	
à former un motif optique de diffraction dans la couche de composé d'oxyde à l'aide d'un processus d'attaque chimique.	
27. Procédé selon la revendication 26, dans lequel la couche comprenant le composé d'oxyde est une structure multicouche constituée de couches de composé d'oxyde alternant avec des couches d'un second composé de fluorure ou des couches d'un oxyde métallique, et les couches de second composé de fluorure ou d'oxyde métallique servent de couches d'arrêt d'attaque dans le processus d'attaque.	
28. Procédé selon la revendication 2 ou la revendication 27, comportant, en outre, l'étape consistant à former une couche antiréfléchissante sur une surface ou sur les deux surfaces de l'élément optique.	

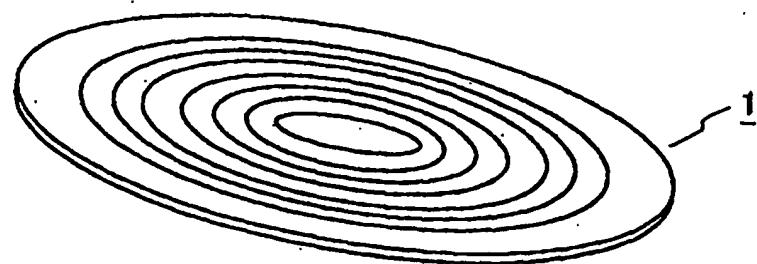


FIG. 1

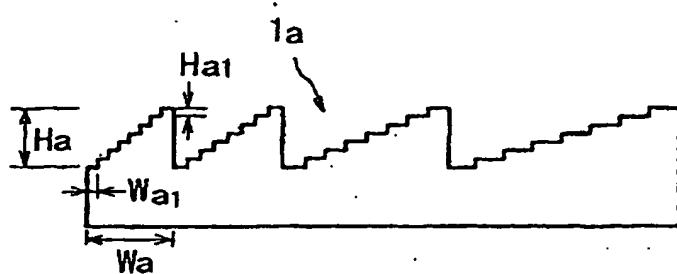


FIG. 2A



FIG. 2B

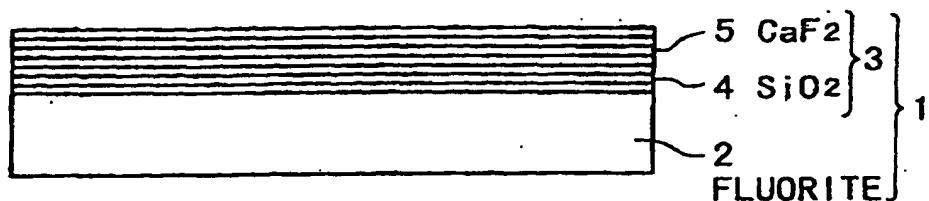


FIG. 3

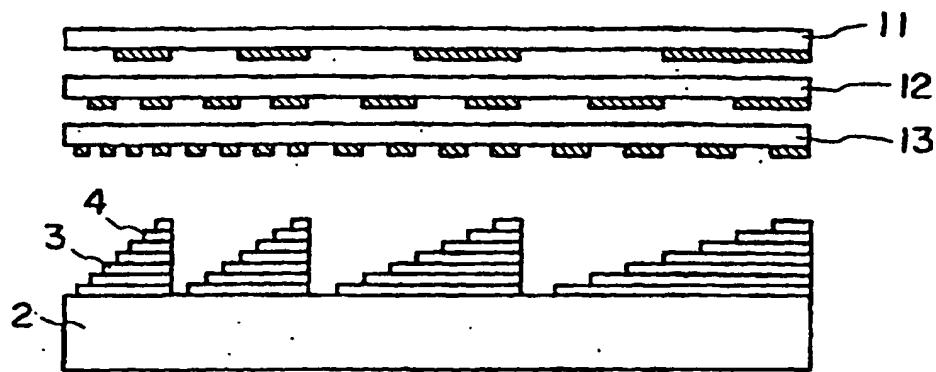


FIG. 4

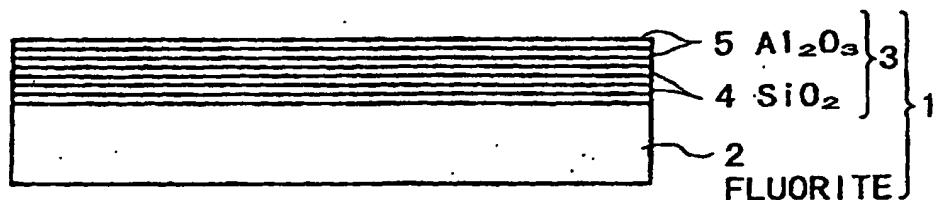


FIG. 5

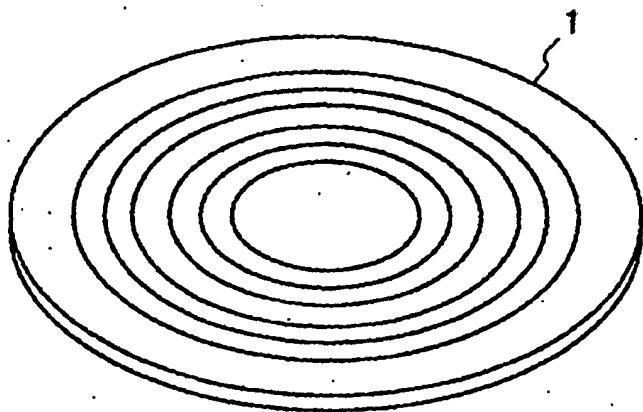


FIG. 6

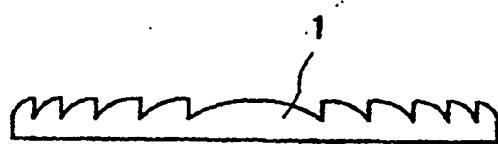


FIG. 7

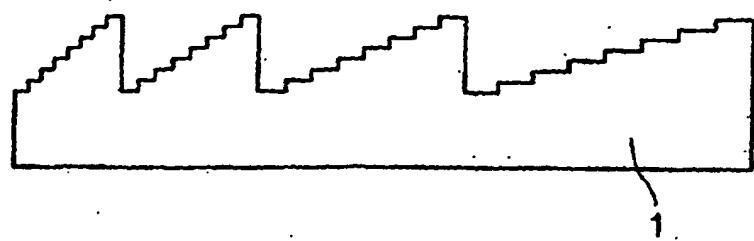


FIG. 8

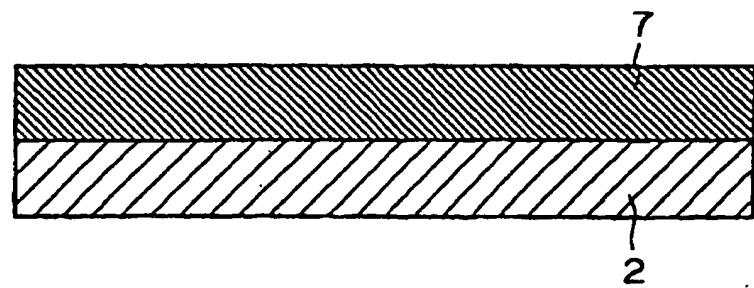


FIG. 9

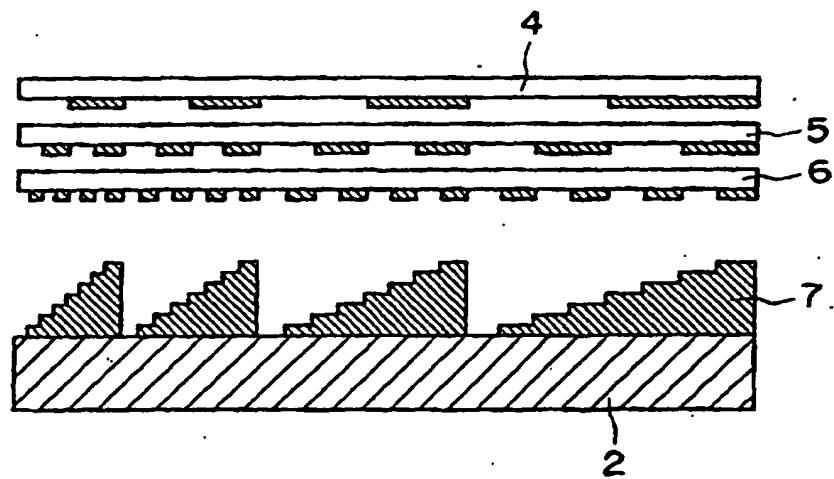


FIG. 10

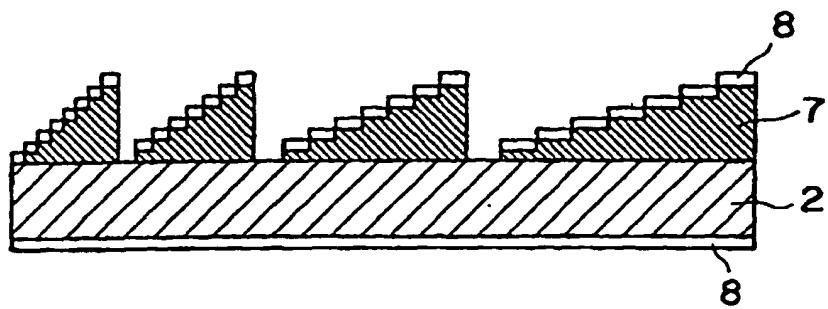


FIG. 11

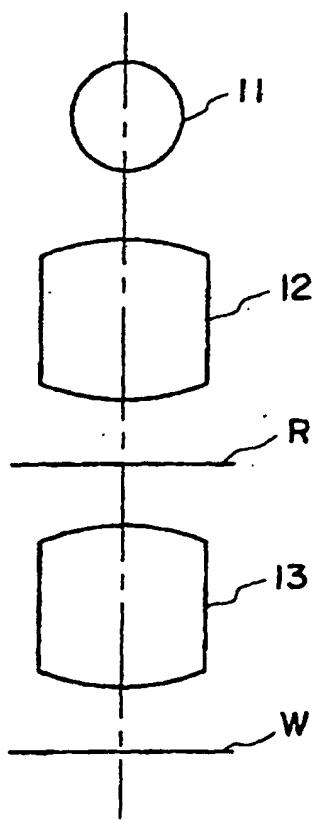


FIG. 12